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DECREASE IN CO<sub>2</sub> CONCENTRATION ABOVE THE TROPOPAUSE

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Department of Physics  
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Denver, Colorado 80210

Contract F19628-68-C-0233

Project No. 8662

Task No. 866201

Work Unit No. 86620101

Scientific Report No. 1

June 1968

This research was sponsored by the Advanced Research Projects Agency  
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Contract Monitor: Charles V. Cunniff  
Optical Physics Laboratory

Prepared for

Air Force Cambridge Research Laboratories  
Office of Aerospace Research  
United States Air Force  
Bedford, Massachusetts



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## ABSTRACT

Comparisons between the  $\text{CO}_2$  telluric absorptions observed in high altitude solar spectra and those predicted on a theoretical basis indicates that the atmospheric concentration of  $\text{CO}_2$  decreases above the tropopause.  $\text{CO}_2$  mixing ratios were determined on the basis of the absorptions observed in the  $2.7\mu$  and  $4.3\mu$  spectral regions. The concentration determined by both bands gives a value of  $2.1 \cdot 10^{-4}$  as the volume concentration of  $\text{CO}_2$  above 17 km as compared with the value of  $3.3 \cdot 10^{-4}$  for the surface concentration.



## 1. INTRODUCTION

It has long been assumed that the concentration of carbon dioxide in the atmosphere is independent of altitude at least through the stratosphere and varies only slightly from its mean value with location and time. A detailed analysis of infrared solar spectra obtained at various altitudes by means of a balloon borne spectrometer system indicates that there is a large decrease in concentration of carbon dioxide above the tropopause.

In previous studies<sup>1,2</sup> the atmospheric absorptions due to  $\text{CO}_2$  in the  $2.7\mu$  and  $4.3\mu$  regions observed at various altitudes were compared with the theoretical absorptions calculated using a number of techniques without arriving at any conclusions concerning the concentration of  $\text{CO}_2$ . Since these earlier publications a number of advances have been made in computers, computational procedures and laboratory data concerning molecular absorption. Additional experimental data have also been obtained. Using the new techniques and the new data it has been possible to determine the concentration of  $\text{CO}_2$  in the lower stratosphere from the observed atmospheric absorptions with sufficient accuracy to show that the concentration decreases significantly above the tropopause.

## 2. EXPERIMENTAL DATA

The high altitude solar spectra used in this study were obtained by means of a balloon borne spectrometer system which is flown in conjunction with a biaxial pointing control which maintains

the solar radiation on the spectrometer entrance slit. The instrumentation has been described in detail in a previous publication.<sup>3</sup> The absorption bands used in this study were the two vibration rotation bands in the vicinity of  $2.7\mu$  and the strong absorption at  $4.3\mu$ . The data concerning the variation of the  $2.7\mu$  absorption in the solar spectrum with altitude above the earth's surface were obtained during a balloon flight made September 30, 1965 from Chico California. Data concerning the variation of the  $4.3\mu$  band with altitude were obtained during a balloon flight made May 14, 1964 from Holloman AFB, New Mexico. During both flights solar spectra were recorded at various altitudes from the ground through 30 km.

### 3. ANALYSIS OF THE ABSORPTIONS

The  $2.7\mu$  band of  $\text{CO}_2$  is overlapped by water vapor absorption bands at the same wavelength, but the decreased amount of water vapor in the atmosphere above the tropopause allows the overlapping to be taken into account. At levels below 11 km however, the water vapor absorptions are large enough to make it impractical to determine the carbon dioxide concentration using this absorption region. At the higher altitudes the  $4.3\mu$  band is not affected by the absorption of other atmospheric gases. Only the region from  $2300 - 2400 \text{ cm}^{-1}$  was used in the determination of the  $\text{CO}_2$  concentration since it is felt that the smaller contributions of isotopic and "hot" states in this region would result in a more accurate determination of the  $\text{CO}_2$  concentration. The great intensity of this band causes the absorption to be almost total, at least over a large part of the

wavelength interval, for altitudes less than 23 km. In view of these limitations the mixing ratio was determined only for altitudes above 11 km, and by use of two different bands above 23 km.

The infrared absorptions considered here depend on the pressure environment and temperature of the absorbing gas. In order to predict theoretically the absorptions to be expected under atmospheric conditions it is necessary to incorporate some techniques for treating the "slant path" calculations. The variation in pressure environment of the gas was treated by breaking up the atmosphere into incremental layers. In each layer the pressure was assumed to be constant and the transmission was calculated for each layer. The temperature dependence of the absorption arises from the dependence of the line strength and half-width on temperature. The overall dependence of the integrated absorbance on temperature is at most as  $T^{\frac{1}{2}}$  for the bands considered here. In view of the slow dependence on temperature the atmospheric temperature was taken to be constant at 236°K. This temperature is within 25°K of the atmospheric temperature for at least 95% of the absorber concentration. In the upper stratosphere the temperature reaches higher values, however, the contribution of the CO<sub>2</sub> in this region to the absorption is small. The error introduced by this constant temperature assumption is small and is a maximum at the lower altitudes. At 30 km the error introduced should be almost zero.

The absorption parameters - line frequencies, strengths, and energies for the 4.3 micron band were generated from the

rotational constants, band centers and band strengths published by Gray.<sup>4</sup> The only modification of these values was the shifting of the band center of the fundamental isotopic state  $^{12}\text{C}^{18}\text{O}_2$  from  $2338.00\text{ cm}^{-1}$  to  $2332.16\text{ cm}^{-1}$  on the basis of a recent paper.<sup>5</sup> The same parameters for the  $2.7\mu$  region were generated from the band constants given by Calfee and Benedict.<sup>6</sup> The values were generated rather than using the listed values. Some errors in line strengths presented by these authors seem to be due to a computer malfunction. This is evident in the fact that in some bands the sum of strengths of the lines is not equal to the listed band strengths.

The calculations were performed on a line by line basis. All the lines in the bands were taken into account, and an extinction coefficient determined at points  $0.001\text{ cm}$  apart. This extinction coefficient took into account the Doppler effects on the Lorentz lines. Once the extinction coefficient was known, the absorption at each point was determined. After degrading this monochromatic absorption by the application of a triangular slit function, the integrated absorption was determined. The application of the slit function reduced the errors which could have occurred at the ends of the interval of integration were it not used.

The accuracy of the method of calculating the absorption to be expected and various absorption parameters was checked by comparing the laboratory spectra given by Burch<sup>7</sup> with those calculated for similar paths and pressures. The result of the comparison is given in Table I. Better agreement is obtained by taking the half-widths of the lines to be  $.07\text{ cm}^{-1}$  at one atmosphere pressure instead of  $.08\text{ cm}^{-1}$  as suggested

by Calfee and Benedict. Because of the superior agreement achieved in the  $3650\text{-}3766\text{ cm}^{-1}$  interval, a subinterval in this region,  $3664\text{-}3766\text{ cm}^{-1}$  was used for the determination of the atmospheric  $\text{CO}_2$  concentration. It should be noted also that the use of a too small value for the half-width of the line would result in too large rather than too small a mixing ratio for the  $\text{CO}_2$ .

The water vapor absorption in the  $2.7\mu$  region was taken into account by what might be described as a reversal of the Curtis-Godson approximation. In normal use of the Curtis-Godson approximation, the amount of absorbing material is known and a scaled pressure is used as though the absorption was due to a constant pressure path through the given amount of absorber. In the present work the integrated absorption in the interval  $3764\text{ cm}^{-1}$  to  $3782\text{ cm}^{-1}$ , which is entirely due to  $\text{H}_2\text{O}$ , was used to determine the amount of water vapor which would have to be present at 30 km altitude to account for the observed value of the integrated absorption. Thus rather than scaling the pressure with a constant amount of absorber the pressure was kept constant and the quantity of absorber was scaled. No physical significance can be attributed to the scaled quantity of absorber, but it can be used to predict the quantity of water vapor absorption in the region of absorption by carbon dioxide. Its validity rests on the same arguments as the Curtis-Godson approximation. It is important to keep in mind that this procedure is only being used at altitudes where the absorption by water vapor alone is much less than that due to carbon dioxide alone. No such procedure is required for the  $4.3\mu$  band since it is not overlapped by other bands in the region of interest here.

The slant path calculation was performed as follows: The atmosphere above a given altitude at which the pressure is  $p$  is made of ten constant pressure layers at pressures  $0.1p, 0.2p, \dots, 0.9p$ , and  $1.0p$ . The mixing ratio was taken as the same in all layers. The lines in the  $2.7\mu$  region were taken to have a pure Lorentz shape in each layer and this shape was then convoluted with the Gaussian shape of a pure Doppler broadened line. The product of the resulting line shape and the absorber concentration was summed over the ten levels. The same procedure was used for the  $4.3\mu$  band except a modified rather than pure Lorentz line shape was used. The shape was

$$k(\nu) = \frac{\alpha / \pi}{(\nu - \nu_0)^2 + \alpha^2} \quad |\nu - \nu_0| < 0.5 \text{ cm}^{-1}$$

$$k(\nu) = \frac{\alpha / \pi \exp[-b|\nu - \nu_0|^a]}{(\nu - \nu_0)^2 + \alpha^2} \quad |\nu - \nu_0| > 0.5 \text{ cm}^{-1}$$

where  $\alpha$  is the half-width of the line,  $\nu_0$  is the frequency of the center of the line and  $a$  &  $b$  are constants. The values of the constants used were  $a=0.46$  and  $b=0.46$ . A line shape of this type would be more accurate for the  $2.7\mu$  band but the values of the constants  $a$  and  $b$  are not known for this band. Calculations have indicated that the error caused by this omission of the modification in the line shape will be small. The errors will be greatest at low altitudes where the contribution of the wings of the lines is more important. The agreement obtained between the two bands at the higher altitudes confirms the validity of use of the pure Lorentz line shape convoluted with the Doppler shape for the upper altitudes. It should again be emphasized that all errors

in line shape (including the possibility of an incorrect value for the half-width) result in too large a mixing ratio rather than too small.

The primary results of the calculations are given in Table II. The integrated absorption between  $3664\text{ cm}^{-1}$  and  $3764\text{ cm}^{-1}$  for the  $2.7\mu$  band and between  $2300\text{ cm}^{-1}$  and  $2400\text{ cm}^{-1}$  for the  $4.3\mu$  band is due to the absorptance along a path making an angle  $\theta$  with zenith from the given altitude. The mixing ratio was determined by performing the calculations described above for different values of the mixing ratio and then interpolating between the values to determine the mixing ratio which would give agreement with the observed value of the integrated absorptance. The variation of mixing ratio with altitude can be seen better in Figure 1 which is a plot of effective mixing ratio vs altitude. The lowest altitude for which an effective mixing ratio was determined is 11.87 km where the mixing ratio has already decreased by 10%. However it should be emphasized that the effective mixing ratio is the mixing ratio which if applied throughout the atmosphere will give the observed value of the integrated absorption. Thus at 11.87 km an effective mixing ratio of  $2.74 \cdot 10^{-4}$  fractional concentration by volume is found but at altitudes above 17 km a value of  $2.15 \cdot 10^{-4}$  is found. This means that the actual mixing ratio at 11.87 km is really greater than  $2.74 \cdot 10^{-4}$  since too large a value of the mixing ratio has been used in the upper layers of the calculation for the 11.87 km case.

If the simplifying assumption is made that the absorption  $A$  is a function of the integral of the atmospheric pressure  $p$  with respect to the optical path  $u$ , that is

$$A = A(R) \quad \text{where } R = \int p du$$

then the mixing ratio versus altitude profile can be approximated. The mixing ratio obtained by assuming that the  $\text{CO}_2$  is uniformly distributed above 17 km and modifying the mixing ratio at lower altitudes so as to give the same value of  $R$  as used in the spectral calculations is shown as the dashed line in Figure 1. It can be seen that the variation in mixing ratio occurs very close to the tropopause.

#### 4. DISCUSSION

Most calculations of slant path transmissions in the past have been done on the basis of the Curtis-Godson approximation. In order to see how this approximation would affect the results obtained, the integrated absorptance in the  $2.7\mu$  region was calculated both by the use of the Curtis-Godson approximation and by the use of the ten layer model with Doppler broadening in each level and a mixing ratio of  $3.0 \cdot 10^{-4}$  in all cases. The integrated absorptances obtained with the Curtis-Godson approximation were too large at the lower altitudes and too small at the upper altitudes. The results are reviewed in Table III. The change required in the effective mixing ratio to bring the Curtis-Godson approximation into agreement with the experimental data is also shown. The differences at the lower altitudes are independent of the Doppler effect and are due to insufficiencies in the approximation while those at the upper altitudes are mainly due to Doppler effects.

No explanation for the decrease in the mixing ratio of carbon dioxide can be offered at this time. Although the



molecular weight of  $\text{CO}_2$  is large the available information concerning gravitational separation indicates that the altitude at which the decrease in mixing ratio occurs is much too low to be due to this effect. The occurrence of the decrease at the tropopause seems to be significant and appears to indicate that the amount of  $\text{CO}_2$  transported through the tropopause is small, or there is some reaction which destroys carbon dioxide in the lower stratosphere.

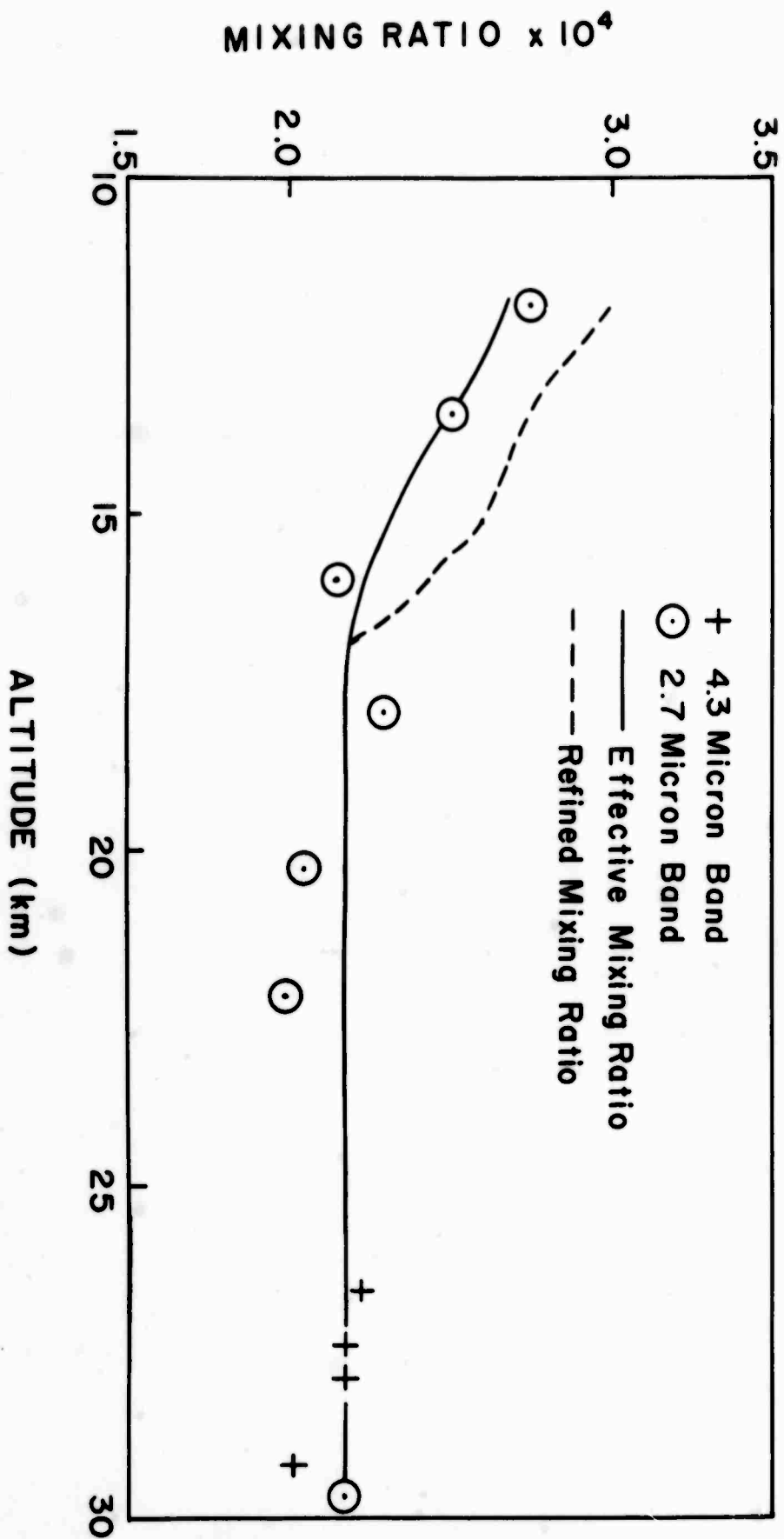


Figure 1. Effective CO<sub>2</sub> mixing ratio as determined from atmospheric absorptions as observed at various altitudes. Procedure for determining the refined mixing ratio is discussed in the text.

Table I

| <u>Interval</u> | <u>Path<br/>Atmos<br/>CM</u> | <u>Equivalent<br/>Pressure<br/>mm Hg</u> | <u>Integrated Absorptance cm<sup>-1</sup></u> |                   | <u>Half-width at<br/>Atmos cm</u> |
|-----------------|------------------------------|------------------------------------------|-----------------------------------------------|-------------------|-----------------------------------|
|                 |                              |                                          | <u>Experimental</u>                           | <u>Calculated</u> |                                   |
| 1               | 50.33                        | 77.52                                    | 67.02                                         | 68.05             | 0.07                              |
| 1               | 50.33                        | 77.52                                    | 67.02                                         | 70.93             | 0.08                              |
| 1               | 50.29                        | 762.05                                   | 104.23                                        | 108.00            | 0.08                              |
| 1               | 16.91                        | 762.05                                   | 78.77                                         | 84.62             | 0.08                              |
| 1               | 0.3047                       | 817.30                                   | 7.16                                          | 9.07              | 0.07                              |
| 1               | 0.3047                       | 817.30                                   | 7.16                                          | 9.34              | 0.08                              |
| 2               | 50.33                        | 77.52                                    | 63.70                                         | 61.73             | 0.07                              |
| 2               | 50.33                        | 77.52                                    | 63.70                                         | 64.03             | 0.08                              |
| 2               | 50.29                        | 762.05                                   | 88.42                                         | 91.17             | 0.08                              |
| 2               | 16.91                        | 762.05                                   | 74.22                                         | 75.43             | 0.08                              |
| 2               | 0.3047                       | 817.30                                   | 10.38                                         | 10.45             | 0.07                              |
| 2               | 0.3047                       | 817.30                                   | 10.38                                         | 10.83             | 0.08                              |

Interval 1: 3490.0 - 3650.8 cm<sup>-1</sup>

Interval 2: 3650.8 - 3766.0 cm<sup>-1</sup>

Table II

| <u>Band</u> | <u>Altitude<br/>km</u> | <u>Sec <math>\theta</math></u> | <u><math>A_{\nu} \text{cm}^{-1}</math></u> | <u>Mixing Ratio <math>\times 10^4</math></u> |
|-------------|------------------------|--------------------------------|--------------------------------------------|----------------------------------------------|
| 2.7         | 11.9                   | 1.43                           | 70.4                                       | 2.74                                         |
| 2.7         | 13.6                   | 1.45                           | 61.5                                       | 2.56                                         |
| 2.7         | 16.9                   | 1.49                           | 42.5                                       | 2.14                                         |
| 2.7         | 18.0                   | 1.51                           | 35.5                                       | 2.29                                         |
| 2.7         | 20.3                   | 1.56                           | 27.0                                       | 2.04                                         |
| 2.7         | 22.2                   | 1.59                           | 23.2                                       | 1.98                                         |
| 4.3         | 26.6                   | 1.78                           | 56.0                                       | 2.22                                         |
| 4.3         | 27.4                   | 1.73                           | 52.0                                       | 2.16                                         |
| 4.3         | 27.9                   | 1.70                           | 50.0                                       | 2.16                                         |
| 4.3         | 29.2                   | 1.63                           | 43.0                                       | 2.01                                         |
| 2.7         | 29.7                   | 1.88                           | 9.5                                        | 2.16                                         |
| 4.3         | 30.4                   | 1.53                           | 37.0                                       | 1.83                                         |

Table III

| <u>Altitude(km)</u> | $A_v \text{ cm}^{-1}$<br><u>Curtis-Godson</u> | $A_v \text{ cm}^{-1}$<br><u>10 Level</u> | Difference in<br><u>Mixing Ratio <math>\times 10^4</math></u> |
|---------------------|-----------------------------------------------|------------------------------------------|---------------------------------------------------------------|
| 11.87               | 70.68                                         | 70.21                                    | -0.10                                                         |
| 13.56               | 63.00                                         | 62.53                                    | -0.09                                                         |
| 16.87               | 45.36                                         | 45.11                                    | -0.04                                                         |
| 18.00               | 39.56                                         | 39.40                                    | -0.03                                                         |
| 20.32               | 30.59                                         | 30.69                                    | 0.01                                                          |
| 22.23               | 25.02                                         | 25.24                                    | 0.05                                                          |
| 29.70               | 10.73                                         | 11.49                                    | 0.51                                                          |

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| 14 | KEY WORDS                       | LINK A |    | LINK B |    | LINK C |    |
|----|---------------------------------|--------|----|--------|----|--------|----|
|    |                                 | ROLE   | WT | ROLE   | WT | ROLE   | WT |
|    | CO <sub>2</sub><br>Mixing Ratio |        |    |        |    |        |    |